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(54) Title: DETERGENT COMPOSITION

(57) Abstract

There is provided an automatic dishwashing detergent composition comprising a high cloud point nonionic surfactant and an amount of water-soluble salt to provide conductivity in deionised water at 25° of greater than 3 milli Siemens/cm.

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Detergent Composition

Technical Field

The present invention relates to a detergent composition comprising at least one high cloud point nonionic surfactant and an amount of water-soluble salt to provide conductivity in deionised water measured at 25°C of greater than 3 milli Siemens/cm.

Background

Although in general detergent compositions employed in automatic dishwashing and fabric laundering may be similar there is at least one distinct difference that is a function of the different washing mechanisms of the dishwashing and fabric laundering machines commonly available in the market. Fabric laundering is normally done in purpose-built machines having a tumbling action, whereas automatic dishwashing appliances use a spray action mechanism. Fabric laundering machines are able to tolerate detergent compositions which produce suds, fabric laundering detergent compositions are thus generally suds producing. By contrast the spray action of dishwashing machines tends to cause sudsing. Suds can easily overflow the low sills of dishwashers and slow down the spray action, which in turn reduces the cleaning action. Fabric laundering detergent compositions are generally understood to be incompatible with use in automatic dishwashing machines.

Detergent compositions generally comprise at least one detergent surfactant. Surfactants can be selected from anionic, nonionic, cationic, zwitterionic or amphoteric. Surfactants are known to provide two distinct functions defined by the cloud point of the particular surfactant. Above the cloud point of the surfactant, the

surfactant tends to become increasingly insoluble and provides a suds suppression function, whereas below the cloud point, the surfactant tends to be soluble, providing a cleaning function. The majority of commonly available surfactants are generally used below their cloud points providing cleaning benefits but also produce suds. Since suds reduce the cleaning action of the automatic dishwasher use of these surfactants is undesirable in automatic dishwashers. Generally, surfactants selected for use in automatic dishwashing are low-sudsing nonionic surfactants.

Low-sudsing nonionic surfactants generally have low cloud points and are therefore generally above their cloud points, providing a suds suppression function, in use in the dishwasher. As described above, surfactants above their cloud point generally provide only limited cleaning benefits, for example spot reduction benefits. Attempts at making use of higher cloud point nonionic surfactants that provide a cleaning function have typically failed due to the unacceptable sudsing of such surfactants.

Despite the prejudice in the art, the Applicant has found that a nonionic surfactant having a high cloud point can be incorporated into an automatic dishwashing detergent composition. In addition, the cleaning performance of the high cloud point surfactant is further improved, especially on cleaning greasy soils (e.g., lipstick) when the conductivity of the wash water of the dishwasher is greater than 3 milli Siemens/cm (measured at 25°C). In a preferred aspect of the present invention the automatic dishwashing detergent composition additionally comprises a suds suppresser and/or more particularly a low cloud point nonionic surfactant.

Summary of the Invention

According to the present invention there is provided an automatic dishwashing detergent composition comprising:

a) one or more high cloud point nonionic surfactants having a cloud point of greater than 40°C; and

b) an amount of water-soluble salt to provide conductivity in deionised water measured at 25°C of greater than 3 milli Siemens/cm.

Detailed Description of the Invention

High Cloud Point Nonionic Surfactant System

High cloud point nonionic surfactants useful in the present invention are present at levels of from 0.1% to 15% of the composition. In general, bleach-stable surfactants are preferred.

The nonionic surfactant of the present invention has a high cloud point. "Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed. Vol.22 pp. 360-379,"Surfactants and Detersive Systems").

The term "high cloud point" nonionic has a cloud point of greater than 40°C, preferably greater than 50°C, and more preferably greater than 60°C. Preferably the nonionic surfactant comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from 8 to 20 carbon atoms, with from 6 to 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis. Suitable high cloud point nonionic surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

It is also preferred for the purposes of the present invention that the high cloud point nonionic surfactant additionally has a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from 9 to 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from 6 to 20 carbon atoms (C_6-C_{20} alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/C11 or C11/C15 branched alcohol ethoxylates, condensed with an average of from 6 to 15 moles, preferably from 6 to 12 moles, and most preferably from 6 to 9 moles of ethylene oxide per

mole of alcohol. Preferably such ethoxylated nonionic surfactants have a narrow ethoxylate distribution relative to the average.

Nonionic surfactants can optionally contain propylene oxide in an amount up to 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Water-Soluble Salt

Suitable water-soluble salts include any known water-soluble salt commonly available and suitable for incorporation into an automatic dishwashing detergent composition. Preferred water-soluble salts dissolve in water, preferably at temperature less than 40°C, more preferably less than 35°C and even more preferably less than 30°C. Most preferably the water-soluble salt dissolves at ambient temperature.

The water-soluble salt is present in an amount such that when dissolved in deionised water it provides conductivity in deionised water measured at 25°C of greater than 3 milli Siemens/cm, preferably greater than 4 milli Siemens/cm, most preferably greater than 4.5 milli Siemens/cm.

Preferred water-soluble salts incorporated into the detergent composition of the present invention include those that readily dissociate in water. Preferred salts include those which provide multi valent dissociated ions, for example the salts of sulphate, nitrate or perborate, however salts that provide dissociated ions with single valency (eg. chloride) may also be used. Preferred salts are those which remain dissociated in water providing sustained conductivity, for example water soluble sulphate salts. However, salts that dissociate but then re-associate with the same and/or other ions to form the same and/or other salts, thus providing only transient conductivity, may also be used. In this embodiment however, it is preferred that several water-soluble salts are used such that a combination of a number of water-soluble salts provide conductivity greater than 3 milli Siemens/cm, preferably greater than 4 milli Siemens/cm, most preferably greater than 4.5 milli Siemens/cm.

Conductivity Measurement method

For the purposes of the present invention, conductivity was measured using a Jenway 4020 conductivity meter calibrated against a standard sample of known conductivity; for example a 0.01M solution of potassium chloride provides conductivity of 1.413 milli Siemens/cm.

A solution comprising 4g of detergent composition in 1 litre of deionised water was prepared. The solution was continuously stirred at a constant rate to aid dissolution of the detergent composition. 60ml samples of the solution are removed at intervals and the conductivity measured using the Jenway 4020 conductivity meter.

Sulphate Salt

A highly preferred water-soluble salt is a water-soluble sulphate salt. Where present, the water-soluble sulphate salt is present at a level of from 0.1% to 40%, more preferably from 1% to 30%, most preferably from 5% to 25% by weight of the compositions.

The water-soluble sulphate salt may be essentially any sulphate salt with any suitable counter cation. Preferred salts are selected from the sulphates of the alkali and alkaline earth metals, particularly sodium sulphate.

Silicate Salt

Another preferred water-soluble salt is a water-soluble silicate salt. Preferably the water-soluble silicate salt is an alkali or alkaline earth metal silicate. A preferred alkali metal silicate is sodium silicate having an $SiO_2:Na_2O$ ratio of from 1.8 to 3.0, preferably from 1.8 to 2.4, most preferably 2.0. Sodium silicate is preferably present at a level of less than 20%, preferably from 1% to 15%, most preferably from 3% to 12% by weight of SiO_2. The alkali metal silicate may be in the form of either the anhydrous salt or a hydrated salt.

Alkali metal silicate whilst providing conductivity in the wash water will also provide alkalinity. Alkalinity is also preferably provided by the presence of sodium metasilicate. Where present the sodium metasilicate is present at a level of at least

0.4%, preferably at least 1%, most preferably at least 1.5%. Sodium metasilicate has a nominal SiO_2 : Na_2O ratio of 1.0. The weight ratio of said sodium silicate to said sodium metasilicate, measured as SiO_2, is preferably from 50:1 to 5:4, more preferably from 15:1 to 2:1, most preferably from 10:1 to 5:2.

Water-soluble salts of Bleaching Agents

Other preferred water-soluble salts include salts of bleaching agents, for example the salts of oxygen-releasing or chloride bleaching agents. Preferred water-soluble include those of perborate and chloride bleaching agents. These and other suitable bleaching agents are described in more detail hereafter.

Suds Suppressers

Particularly preferred components of the detergent composition are compounds for reducing or suppressing the formation of suds. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressers, and suds suppressers are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppresser of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppresser typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressers. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to

tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of -40°C and 50°C, and a minimum boiling point not less than 110 C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from 12 to 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

(i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;

(ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(CH_3)_3SiO_{1/2}$ units of SiO_2 units in a ratio of from $(CH_3)_3$ $SiO_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and

(iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

In a preferred embodiment of the present invention, the detergent composition additionally comprises a low cloud point nonionic surfactant sud suppressor. As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than 20°C, and most preferably less than 10°C. Typical low cloud point nonionic surfactants include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene

(PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B series of nonionics, described in WO 94/22800, published October 13, 1994 by Olin Corporation) and ether-capped poly(oxyalkylated) alcohol surfactants described in more detail later.

Low cloud point nonionic surfactants may comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC® 25R2 and TETRONIC® 702, Such surfactants are typically useful herein as low cloud point nonionic surfactants.

Where the detergent composition of the present invention comprises a low cloud point as well as a high cloud point surfactant the surfactants are combined in a weight ratio preferably within the range of from 10:1 to 1:10.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C_6-C_{16} alkyl alcohols having a C_1-C_{16} chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry or dishwashing machines, suds should not form to the extent that they either overflow the washing machine or negatively affect the washing mechanism of the dishwasher. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select

an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry or dishwashing detergents for use in automatic laundry or dishwashing machines.

The compositions herein will generally comprise from 0% to 10% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to 5%, by weight, of the detergent composition. Preferably, from 0.5% to 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from 0.01% to 1% of silicone suds suppressor is used, more preferably from 0.25% to 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any optional materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from 0.1% to 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from 0.01% to 5.0%, although higher levels can be used. The low cloud point nonionic surfactant suds suppressors are typically used at 0.1%-15% by weight of the finished compositions

Process

The detergent composition described herein is prepared by conventional methods, in that particulate components are premixed in a suitable mixer and liquid components are applied to, preferably sprayed onto the premix to form the detergent composition. Particulate components may be prepared by any known method for example spray drying granulation or agglomeration. Suitable mixers may be batch or continuous mixers and include, but are not limited to pan, rotary drum and vertical blender types.

A particularly preferred process for preparing the detergent composition described herein is described in co-pending GB Patent Application (Attorney docket number CM 1572F).

Detergent Composition

The detergent composition described herein may include a variety of different ingredients including builder compounds, additional surfactants, enzymes, bleaching agents, alkalinity sources, lime soap dispersants, organic polymeric compounds including polymeric dye transfer inhibiting agents, crystal growth inhibitors, heavy metal ion sequestrants, metal ion salts, enzyme stabilisers, corrosion inhibitors, suds suppressors, solvents, fabric softening agents, optical brighteners and hydrotropes.

Highly preferred components of the detergent composition as described earlier include a builder compound, a surfactant, an enzyme and a bleaching agent.

Builder Compound

The detergent compositions of the present invention preferably contain a builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Where water-soluble builders compounds are present in salt form, the salt may also provide conductivity in the wash water. Such builder compounds include salts of polycarboxylates, carbonates, bicarbonates, borates, phosphates.

Water-Soluble Builder Compound

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and

carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less that about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Highly preferred builder compounds for use in the present invention are water-soluble phosphate builders. Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerisation ranges from about 6 to 21, and salts of phytic acid.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially Soluble or Insoluble Builder Compound

The compositions of the present invention may contain a partially soluble or insoluble builder compound. Partially soluble and insoluble builder compounds are particularly suitable for use in detegent compositions prepared for use in laundry cleaning methods. Examples of partially water soluble builders include the crystalline layered silicates as disclosed for example, in EP-A-0164514, DE-A-3417649 and DE-A-3742043. Preferred are the crystalline layered sodium silicates of general formula

$$NaMSi_xO_{2+1} \cdot yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type preferably have a two dimensional 'sheet' structure, such as the so called δ-layered structure, as described in EP 0 164514 and EP 0 293640.
Methods for preparation of crystalline layered silicates of this type are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2,3 or 4 and is preferably 2.

The most preferred crystalline layered sodium silicate compound has the formula δ-$Na_2Si_2O_5$, known as NaSKS-6 (trade name), available from Hoechst AG.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material as described in PCT Patent Application No. WO92/18594. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof, with citric acid being preferred.

Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicates include the aluminosilicate zeolites having the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. xH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof.

A preferred method of synthesizing aluminosilicate zeolites is that described by Schoeman et al (published in Zeolite (1994) 14(2), 110-116), in which the author describes a method of preparing colloidal aluminosilicate zeolites. The colloidal aluminosilicate zeolite particles should preferably be such that no more than 5% of the particles are of size greater than 1µm in diameter and not more than 5% of particles are of size less then 0.05 µm in diameter. Preferably the aluminosilicate zeolite particles have an average particle size diameter of between 0.01µm and 1µm, more preferably between 0.05 µm and 0.9 µm, most preferably between 0.1µm and 0.6 µm.

Zeolite A has the formula

$$Na_{12} [AlO_2)_{12} (SiO_2)_{12}]. xH_2O$$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86} [(AlO_2)_{86}(SiO_2)_{106}]. 276\ H_2O$. Zeolite MAP, as disclosed in EP-B-384,070 is a preferred zeolite builder herein.

Preferred aluminosilicate zeolites are the colloidal aluminosilicate zeolites. When employed as a component of a detergent composition colloidal aluminosilicate zeolites, especially colloidal zeolite A, provide enhanced builder performance in terms of providing improved stain removal. Enhanced builder performance is also seen in terms of reduced fabric encrustation and improved fabric whiteness maintenance; problems believed to be associated with poorly built detergent compositions.

A surprising finding is that mixed aluminosilicate zeolite detergent compositions comprising colloidal zeolite A and colloidal zeolite Y provide equal calcium ion sequestration performance versus an equal weight of commercially available zeolite A. Another surprising finding is that mixed aluminosilicate zeolite detergent

compositions, described above, provide improved magnesium ion sequestration performance versus an equal weight of commercially available zeolite A.

Additional Surfactant

The detergent composition of the present invention may comprise an additional surfactant. Suitable surfactants are selected from anionic, cationic, nonionic ampholytic and zwitterionic surfactants and mixtures thereof. Automatic dishwashing machine products should be low foaming in character, thus the foaming of the surfactant system for use in dishwashing methods is preferably suppressed. The total surfactant is typically present at a level of from 0.2% to 30% by weight, more preferably from 0.5% to 10% by weight, most preferably from 1% to 5% by weight of the compositions.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31,1981. A listing of surfactants typically included in automatic dishwashing detergent compositions is given for example, in EP-A-0414 549 and PCT Applications No.s WO 93/08876 and WO 93/08874.

Nonionic Surfactant

Essentially any nonionic surfactants useful for detersive purposes can be included in the compositions. Preferred, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic Ethoxylated Alcohol Surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20

carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

End-Capped Alkyl Alkoxylate Surfactant

A suitable endcapped alkyl alkoxylate surfactant is the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

$$R_1O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_y[CH_2CH(OH)R_2] \quad (I)$$

wherein R_1 is a linear or branched, aliphatic hydrocarbon radical having from about 4 to about 18 carbon atoms; R_2 is a linear or branched aliphatic hydrocarbon radical having from about 2 to about 26 carbon atoms; x is an integer having an average value of from 0.5 to about 1.5, more preferably about 1; and y is an integer having a value of at least about 15, more preferably at least about 20.

Preferably, the surfactant of formula I, at least about 10 carbon atoms in the terminal epoxide unit $[CH_2CH(OH)R_2]$. Suitable surfactants of formula I, according to the present invention, are Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

Ether-capped poly(oxyalkylated) alcohols

Preferred surfactants for use herein include ether-capped poly(oxyalkylated) alcohols having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 30, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12, and more preferably 1 to 5.

R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 6 to 22 carbon atoms with 8 to 18 carbon atoms being most preferred. H or a linear aliphatic hydrocarbon radical having from 1 to 2 carbon atoms is most preferred for R^3. Preferably, x is an integer having an average value of from 1 to 20, more preferably from 6 to 15.

As described above, when, in the preferred embodiments, and x is greater than 2, R^3 may be the same or different. That is, R^3 may vary between any of the alklyeneoxy units as described above. For instance, if x is 3, R^3may be be selected to form ethlyeneoxy(EO) or propyleneoxy(PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher integer value for x and include, for example, mulitple (EO) units and a much small number of (PO) units.

Particularly preferred surfactants as described above include those that have a low cloud point of less than 20°C. These low cloud point surfactants may then be employed in conjunction with a high cloud point surfactant as described in detail below for superior grease cleaning benefits.

Most preferred ether-capped poly(oxyalkylated) alcohol surfactants are those wherein k is 1 and j is 1 so that the surfactants have the formula:

$$R^1O[CH_2CH(R^3)O]_xCH_2CH(OH)CH_2OR^2$$

where R^1, R^2 and R^3 are defined as above and x is an integer with an average value of from 1 to 30, preferably from 1 to 20, and even more preferably from 6 to 18. Most preferred are surfactants wherein R^1 and R^2 range from 9 to 14, R^3 is H forming ethyleneoxy and x ranges from 6 to 15.

The ether-capped poly(oxyalkylated) alcohol surfactants comprise three general components, namely a linear or branched alcohol, an alkylene oxide and an alkyl ether end cap. The alkyl ether end cap and the alcohol serve as a hydrophobic, oil-soluble portion of the molecule while the alkylene oxide group forms the hydrophilic, water-soluble portion of the molecule.

These surfactants exhibit significant improvements in spotting and filming characteristics and removal of greasy soils, when used in conjunction with high cloud point surfactants, relative to conventional surfactants.

Generally speaking, the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention may be produced by reacting an aliphatic alcohol with an epoxide to form an ether which is then reacted with a base to form a second epoxide. The second epoxide is then reacted with an alkoxylated alcohol to form the novel compounds of the present invention. Examples of methods of preparing the ether-capped poly(oxyalkylated) alcohol surfactants are described below:

Preparation of $C_{12/14}$ alkyl glycidyl ether

A $C_{12/14}$ fatty alcohol (100.00 g, 0.515 mol.) and tin (IV) chloride (0.58 g, 2.23 mmol, available from Aldrich) are combined in a 500 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 °C. Epichlorhydrin (47.70 g, 0.515 mol, available from Aldrich) is added dropwise so as to keep the temperature between 60-65 °C. After stirring an additional hour at 60 °C, the mixture is cooled to room temperature. The mixture is treated with a 50% solution of sodium hydroxide (61.80 g, 0.773 mol, 50%) while being stirred mechanically. After addition is completed, the mixture is heated to 90 °C for 1.5 h, cooled, and filtered with the aid of ethanol. The filtrate is separated and the organic phase is washed with water (100 mL), dried over $MgSO_4$, filtered, and concentrated. Distillation of the oil at 100-120 °C (0.1 mm Hg) providing the glycidyl ether as an oil.

Preparation of $C_{12/14}$ alkyl-$C_{9/11}$ ether capped alcohol surfactant

Neodol® 91-8 (20.60 g, 0.0393 mol ethoxylated alcohol available from the Shell chemical Co.) and tin (IV) chloride (0.58 g, 2.23 mmol) are combined in a 250 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 ° C at which point $C_{12/14}$ alkyl glycidyl ether (11.00 g, 0.0393 mol) is added dropwise over 15 min. After stirring for 18 h at 60 °C, the mixture is cooled to room temperature and dissolved in an equal portion of dichloromethane. The solution is passed through a 1 inch pad of silica gel while eluting with dichloromethane. The filtrate is concentrated by rotary evaporation and then stripped in a kugelrohr oven (100 °C, 0.5 mm Hg) to yield the surfactant as an oil.

Nonionic Ethoxylated/Propoxylated Fatty Alcohol Surfactant

The ethoxylated C_6-C_{18} fatty alcohols and C_6-C_{18} mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C_{10}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO Condensates with Propylene Glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO Condensation Products with Propylene Oxide/Ethylene Diamine Adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Anionic Surfactant

Essentially any anionic surfactants useful for detersive purposes are suitable. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic Sulfate Surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10}-C_{18} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic Sulfonate Surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic Carboxylate Surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_x CH_2COO^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali Metal Sarcosinate Surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group,

R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Amphoteric Surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic Surfactants

Cationic ester surfactants used in this invention are preferably water dispersible compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group. Other suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Enzymes

The detergent compositions described herein may comprise an enzyme. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which disclose fungal cellulases produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800. Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ˜43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases

for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*,

e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^{R} and Lipomax^{R} (Gist-Brocades) and Lipolase^{R} and Lipolase Ultra^{R}(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from Bacillus in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine

replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994.

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo

Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971. Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Bleaching Agent

A highly preferred component of the detergent composition is a bleaching agent. Suitable bleaching agents include chlorine and oxygen-releasing bleaching agents.

In one preferred aspect the oxygen-releasing bleaching agent contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred aspect a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic Perhydrate Bleaches

The compositions in accord with the invention preferably include a hydrogen peroxide source, as an oxygen-releasing bleach. Suitable hydrogen peroxide sources include the inorganic perhydrate salts.

The inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates for inclusion in compositions in accordance with the invention. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. Sodium percarbonate, being a hydrogen peroxide addition compound tends on dissolution to release the hydrogen peroxide quite rapidly which can increase the tendency for localised high bleach concentrations to arise. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in-product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material providing in product stability, comprises sodium silicate of $SiO_2 : Na_2O$ ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of SiO_2 by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating. Coatings that contain silicate and borate salts or boric acids or other inorganics are also suitable.

Other coatings which contain waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility in the compositions herein.

Peroxyacid Bleach Precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as

$$X-\overset{\mathrm{O}}{\overset{\|}{C}}-L$$

where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is

$$X-\overset{\mathrm{O}}{\overset{\|}{C}}-OOH$$

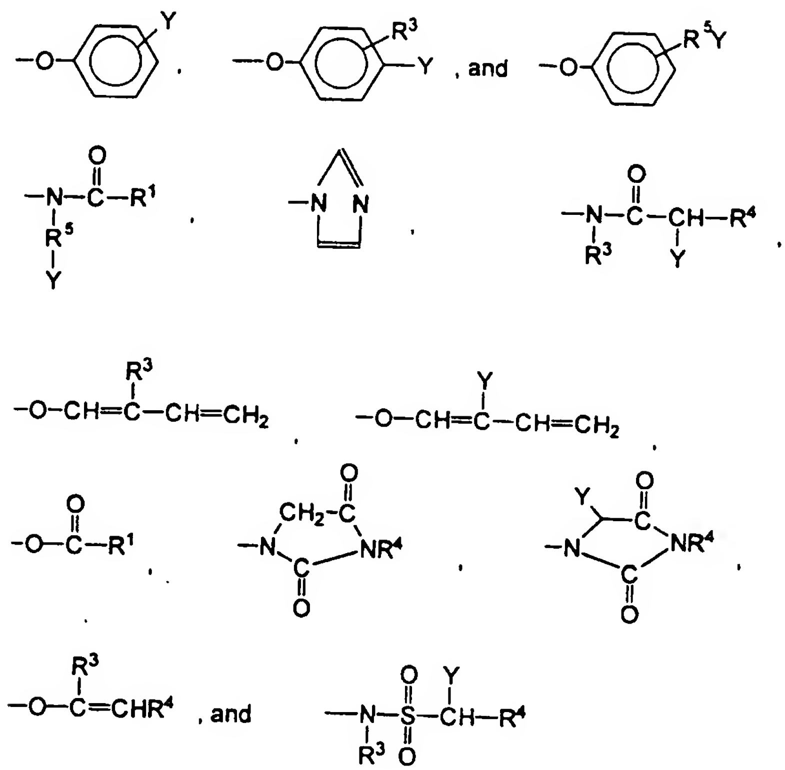
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 10% by weight, most preferably from 1.5% to 5% by weight of the compositions.

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving Groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilise for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



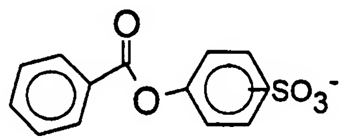
and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, R^5 is an alkenyl chain containing from 1 to 8 carbon atoms and Y is H or a solubilizing group. Any of R^1, R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O{<}{-}{-}N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

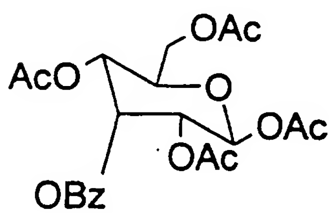
Perbenzoic Acid Precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis.

Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



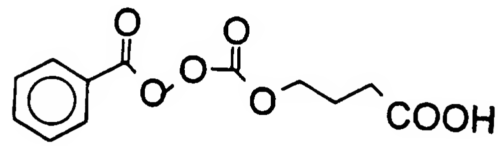
Also suitable are the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:



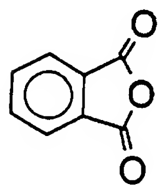
Ac = COCH3; Bz = Benzoyl

Perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

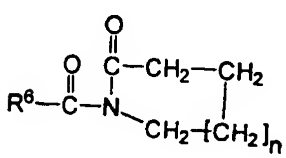
Other perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:



Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:



Suitable N-acylated lactam perbenzoic acid precursors have the formula:



wherein n is from 0 to 8, preferably from 0 to 2, and R^6 is a benzoyl group.

Perbenzoic Acid Derivative Precursors

Perbenzoic acid derivative precursors provide substituted perbenzoic acids on perhydrolysis.

Suitable substituted perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the benzoyl group is substituted by essentially any non-positively charged (i.e.; non-cationic) functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl and amide groups.

A preferred class of substituted perbenzoic acid precursor compounds are the amide substituted compounds of the following general formulae:

$$R^1-\underset{O}{C}-\underset{R^5}{N}-R^2-\underset{O}{C}-L \qquad \text{or} \qquad R^1-\underset{R^5}{N}-\underset{O}{C}-R^2-\underset{O}{C}-L$$

wherein R^1 is an aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an arylene, or alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be aryl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Cationic Peroxyacid Precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the compositions as a salt with a suitable anion, such as for example a halide ion or a methylsulfate ion.

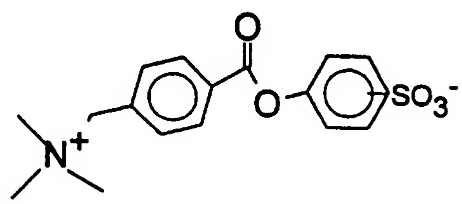
The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl

percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter

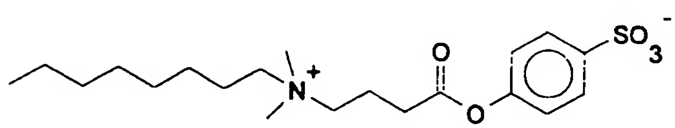
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

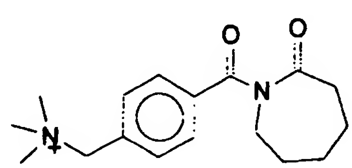
A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



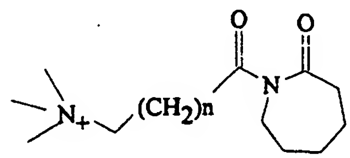
A preferred cationically substituted alkyl oxybenzene sulfonate has the formula:



Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



Other preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene alkyl caprolactams:



where n is from 0 to 12, particularly from 1 to 5.

Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Alkyl Percarboxylic Acid Bleach Precursors

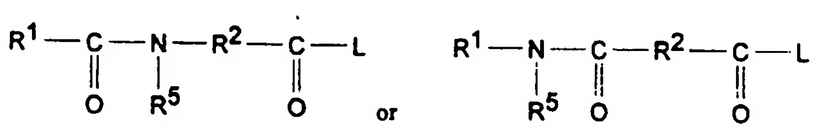
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N^1N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and penta acetyl glucose.

Amide Substituted Alkyl Peroxyacid Precursors

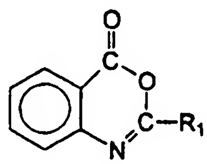
Amide substituted alkyl peroxyacid precursor compounds are also suitable, including those of the following general formulae:



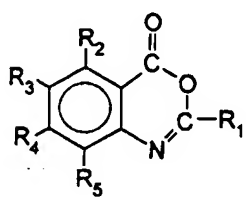
wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Benzoxazin Organic Peroxyacid Precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

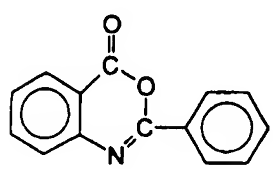


including the substituted benzoxazins of the type



wherein R_1 is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R_2, R_3, R_4, and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxyl, amino, alkyl amino, $COOR_6$ (wherein R_6 is H or an alkyl group) and carbonyl functions.

An especially preferred precursor of the benzoxazin-type is:

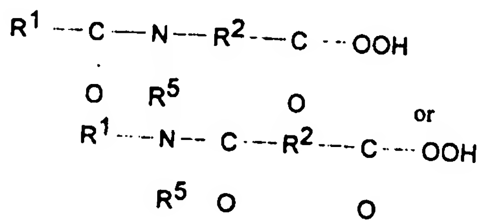


Preformed Organic Peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed

organic peroxyacid , typically at a level of from 0.5% to 25% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid, and diperoxyhexadecanedioc acid. Dibenzoyl peroxide is a preferred organic peroxyacid herein. Mono- and diperazelaic acid, mono- and diperbrassylic acid, and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Metal-Containing Bleach Catalyst

Compositions comprising a bleach described herein may additionally contain a metal containing bleach catalyst as a preferred component. Preferably the metal containing

bleach catalyst is a transition metal containing bleach catalyst, more preferably a manganese or cobalt-containing bleach catalyst.

A suitable type of bleach catalyst is a catalyst comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Preferred types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7\text{-triazacyclononane})_4\text{-}(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-
triazacyclononane, and mixtures thereof.

The bleach catalysts useful in the compositions herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $Mn(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})(OCH_3)_3\text{-}(PF_6)$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulsitol, mannitol, xylithol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:

$$\begin{array}{c} \quad R^2 \quad R^3 \\ R^1\text{-N=C-B-C=N-}R^4 \end{array}$$

wherein R^1, R^2, R^3, and R^4 can each be selected from H, substituted alkyl and aryl groups such that each R^1-N=C-R^2 and R^3-C=N-R^4 form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S. CR^5R^6, NR^7 and C=O, wherein R^5, R^6, and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl_2, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, Co(2,2-bispyridylamine)$_2O_2ClO_4$, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Preferred examples include binuclear Mn complexes with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]\text{-}(ClO_4)_3$.

While the structures of the bleach-catalyzing manganese complexes of the present invention have not been elucidated, it may be speculated that they comprise chelates or other hydrated coordination complexes which result from the interaction of the carboxyl and nitrogen atoms of the ligand with the manganese cation. Likewise, the oxidation state of the manganese cation during the catalytic process is not known with certainty, and may be the (+II), (+III), (+IV) or (+V) valence state. Due to the ligands' possible six points of attachment to the manganese cation, it may be reasonably speculated that multi-nuclear species and/or "cage" structures may exist in

the aqueous bleaching media. Whatever the form of the active Mn·ligand species which actually exists, it functions in an apparently catalytic manner to provide improved bleaching performances on stubborn stains such as tea, ketchup, coffee, wine, juice, and the like.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Other preferred examples include cobalt (III) catalysts having the formula:

$$Co[(NH_3)_nM'_mB'_bT'_tQ_qP_p]\ Y_y$$

wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and n + m + 2b + 3t + 4q + 5p = 6; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, nitrate, nitrite, sulfate, citrate, acetate, carbonate, and combinations thereof; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining co-ordination sites stabilise the cobalt under automatic dishwashing

conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts (preferably less than about 0.2 volts) versus a normal hydrogen electrode.

Preferred cobalt catalysts of this type have the formula:

$$[Co(NH_3)_n(M')_m]\ Y_y$$

wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); m+n = 6; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[Co(NH_3)_5Cl]\ Y_y$, and especially $[Co(NH_3)_5Cl]Cl_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\ T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand co-ordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 $M^{-1}\ s^{-1}$ (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I_3^-, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^-, BF_4^-, $B(Ph)_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, etc. Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F^-, SO_4^{-2}, NCS^-, SCN^-, $S_2O_3^{-2}$, NH_3, PO_4^{3-}, and carboxylates (which preferably are mono-carboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, $HOC(O)CH_2C(O)O$-, etc.) Preferred M moieties are substituted and unsubstituted C_1-C_{30} carboxylic acids having the formulas:

$$RC(O)O-$$

wherein R is preferably selected from the group consisting of hydrogen and C_1-C_{30} (preferably C_1-C_{18}) unsubstituted and substituted alkyl, C_6-C_{30} (preferably C_6-C_{18}) unsubstituted and substituted aryl, and C_3-C_{30} (preferably C_5-C_{18}) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of $-NR'_3$, $-NR'_4{}^+$, $-C(O)OR'$, $-OR'$, $-C(O)NR'_2$, wherein R' is selected from the group consisting of hydrogen and C_1-C_6 moieties. Such substituted R therefore include the moieties $-(CH_2)_nOH$ and $-(CH_2)_nNR'_4{}^+$, wherein n is an integer from 1 to about 16, preferably from about 2 to about 10, and most preferably from about 2 to about 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl,

straight or branched C_4-C_{12} alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as k_{OH}) for cobalt pentaamine catalysts complexed with oxalate (k_{OH}= 2.5×10^{-4} M^{-1} s^{-1} (25°C)), NCS^- (k_{OH}= 5.0×10^{-4} M^{-1} s^{-1} (25°C)), formate (k_{OH}= 5.8×10^{-4} M^{-1} s^{-1} (25°C)), and acetate (k_{OH}= 9.6×10^{-4} M^{-1} s^{-1} (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]\ T_y$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article hereinbefore and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952); as well as the synthesis examples provided hereinafter.

These catalysts may be coprocessed with adjunct materials so as to reduce the color impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

Hydrocarbon Oils

Another preferred detergent component for use in the present invention is a hydrocarbon oil, typically a predominantly long chain, aliphatic hydrocarbons having a number of carbon atoms in the range of from 20 to 50; preferred hydrocarbons are saturated and/or branched; preferred hydrocarbon oil selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of from 1:10 to 2:1, preferably from 1:5 to 1:1. A preferrred hydrocarbon oil is paraffin. A paraffin oil meeting the characteristics as outlined above, having a ratio of cyclic to noncyclic hydrocarbons of about 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Water-Soluble Bismuth Compound

The compositions of the may contain a water-soluble bismuth compound, preferably present at a level of from 0.005% to 20%, more preferably from 0.01% to 5%, most preferably from 0.1% to 1% by weight of the compositions.

The water-soluble bismuth compound may be essentially any salt or complex of bismuth with essentially any inorganic or organic counter anion. Preferred inorganic bismuth salts are selected from the bismuth trihalides, bismuth nitrate and bismuth phosphate. Bismuth acetate and citrate are preferred salts with an organic counter anion.

Bismuth salts are preferred components of the detergent compositions described herein, in that they may additionally provide conductivity.

Corrosion Inhibitor Compound

The compositions of the present invention may contain corrosion inhibitors preferably selected from organic silver coating agents, particularly paraffin, nitrogen-

containing corrosion inhibitor compounds and Mn(II) compounds, particularly Mn(II) salts of organic ligands.

Organic silver coating agents are described in PCT Publication No. WO94/16047 and copending European application No. EP-A-690122. Nitrogen-containing corrosion inhibitor compounds are disclosed in copending European Application no. EP-A-634,478. Mn(II) compounds for use in corrosion inhibition are described in copending European Application No. EP-A-672 749.

Organic silver coating agent may be incorporated at a level of from 0.05% to 10%, preferably from 0.1% to 5% by weight of the total composition.

The functional role of the silver coating agent is to form 'in use' a protective coating layer on any silverware components of the washload to which the compositions of the invention are being applied. The silver coating agent should hence have a high affinity for attachment to solid silver surfaces, particularly when present in as a component of an aqueous washing and bleaching solution with which the solid silver surfaces are being treated.

Suitable organic silver coating agents herein include fatty esters of mono- or polyhydric alcohols having from 1 to about 40 carbon atoms in the hydrocarbon chain.

The fatty acid portion of the fatty ester can be obtained from mono- or poly-carboxylic acids having from 1 to about 40 carbon atoms in the hydrocarbon chain. Suitable examples of monocarboxylic fatty acids include behenic acid, stearic acid, oleic acid, palmitic acid, myristic acid, lauric acid, acetic acid, propionic acid, butyric acid, isobutyric acid, Valerie acid, lactic acid, glycolic acid and β,β'-dihydroxyisobutyric acid. Examples of suitable polycarboxylic acids include: n-butyl-malonic acid, isocitric acid, citric acid, maleic acid, malic acid and succinic acid.

The fatty alcohol radical in the fatty ester can be represented by mono- or polyhydric alcohols having from 1 to 40 carbon atoms in the hydrocarbon chain. Examples of suitable fatty alcohols include; behenyl, arachidyl, cocoyl, oleyl and lauryl alcohol,

ethylene glycol, glycerol, ethanol, isopropanol, vinyl alcohol, diglycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan.

Preferably, the fatty acid and/or fatty alcohol group of the fatty ester adjunct material have from 1 to 24 carbon atoms in the alkyl chain.

Preferred fatty esters herein are ethylene glycol, glycerol and sorbitan esters wherein the fatty acid portion of the ester normally comprises a species selected from behenic acid, stearic acid, oleic acid, palmitic acid or myristic acid.

The glycerol esters are also highly preferred. These are the mono-, di- or tri-esters of glycerol and the fatty acids as defined above.

Specific examples of fatty alcohol esters for use herein include: stearyl acetate, palmityl di-lactate, cocoyl isobutyrate, oleyl maleate, oleyl dimaleate , and tallowyl proprionate. Fatty acid esters useful herein include: xylitol monopalmitate, pentaerythritol monostearate, sucrose monostearate, glycerol monostearate, ethylene glycol monostearate, sorbitan esters. Suitable sorbitan esters include sorbitan monostearate, sorbitan palmitate, sorbitan monolaurate, sorbitan monomyristate, sorbitan monobehenate, sorbitan mono-oleate, sorbitan dilaurate, sorbitan distearate, sorbitan dibehenate, sorbitan dioleate, and also mixed tallowalkyl sorbitan mono- and di-esters.

Glycerol monostearate, glycerol mono-oleate, glycerol monopalmitate, glycerol monobehenate, and glycerol distearate are preferred glycerol esters herein.

Suitable organic silver coating agents include triglycerides, mono or diglycerides, and wholly or partially hydrogenated derivatives thereof, and any mixtures thereof. Suitable sources of fatty acid esters include vegetable and fish oils and animal fats. Suitable vegetable oils include soy bean oil, cotton seed oil, castor oil, olive oil, peanut oil, safflower oil, sunflower oil, rapeseed oil, grapeseed oil, palm oil and corn oil.

Waxes, including microcrystalline waxes are suitable organic silver coating agents herein. Preferred waxes have a melting point in the range from about 35°C to about 110°C and comprise generally from 12 to 70 carbon atoms. Preferred are petroleum

waxes of the paraffin and microcrystalline type which are composed of long-chain saturated hydrocarbon compounds.

Alginates and gelatin are suitable organic silver coating agents herein.

Dialkyl amine oxides such as C_{12}-C_{20} methylamine oxide, and dialkyl quaternary ammonium compounds and salts, such as the C_{12}-C_{20} methylammonium halides are also suitable.

Other suitable organic silver coating agents include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000, polyethylene glycols (PEG) with an average molecular weight of from 600 to 10,000, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, and cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose are examples of such polymeric materials.

Certain perfume materials, particularly those demonstrating a high substantivity for metallic surfaces, are also useful as the organic silver coating agents herein.

Polymeric soil release agents can also be used as an organic silver coating agent.

Suitable polymeric soil release agents include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C_4-C_6 alkylene or oxy C_4-

C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C_4-C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2CH_2O$-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful herein also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C_1-C_4 alkyl and C_4 hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al.

Another suitable soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another suitable polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000.

Another suitable polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink. Other polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoarolyl, end-capped terephthalate esters.

Another soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate.

A preferred organic silver coating agent is a paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from 20 to 50; preferred paraffin oil selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of from 1:10 to 2:1, preferably from 1:5 to 1:1. A paraffin oil meeting these characteristics, having a ratio of cyclic to noncyclic hydrocarbons of about 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Nitrogen-Containing Corrosion Inhibitor Compounds

Suitable nitrogen-containing corrosion inhibitor compounds include imidazole and derivatives thereof such as benzimidazole, 2-heptadecyl imidazole and those imidazole derivatives described in Czech Patent No. 139, 279 and British Patent GB-A-1,137,741, which also discloses a method for making imidazole compounds.

Also suitable as nitrogen-containing corrosion inhibitor compounds are pyrazole compounds and their derivatives, particularly those where the pyrazole is substituted in any of the 1, 3, 4 or 5 positions by substituents R_1, R_3, R_4 and R_5 where R_1 is any of H, CH_2OH, $CONH_3$, or $COCH_3$, R_3 and R_5 are any of C_1-C_{20} alkyl or hydroxyl, and R_4 is any of H, NH_2 or NO_2.

Other suitable nitrogen-containing corrosion inhibitor compounds include benzotriazole, 2-mercaptobenzothiazole, 1-phenyl-5-mercapto-1,2,3,4-tetrazole, thionalide, morpholine, melamine, distearylamine, stearoyl stearamide, cyanuric acid, aminotriazole, aminotetrazole and indazole.

Nitrogen-containing compounds such as amines, especially distearylamine and ammonium compounds such as ammonium chloride, ammonium bromide, ammonium sulphate or diammonium hydrogen citrate are also suitable.

Mn(II) Corrosion Inhibitor Compounds

The compositions may contain an Mn(II) corrosion inhibitor compound. The Mn(II) compound is preferably incorporated at a level of from 0.005% to 5% by weight, more preferably from 0.01% to 1%, most preferably from 0.02% to 0.4% by weight of the compositions. Preferably, the Mn(II) compound is incorporated at a level to provide from 0.1 ppm to 250 ppm, more preferably from 0.5 ppm to 50 ppm, most preferably from 1 ppm to 20 ppm by weight of Mn(II) ions in any bleaching solution.

The Mn (II) compound may be an inorganic salt in anhydrous, or any hydrated forms. Suitable salts include manganese sulphate, manganese carbonate, manganese phosphate, manganese nitrate, manganese acetate and manganese chloride. The Mn(II) compound may be a salt or complex of an organic fatty acid such as manganese acetate or manganese stearate.

The Mn(II) compound may be a salt or complex of an organic ligand. In one preferred aspect the organic ligand is a heavy metal ion sequestrant. In another preferred aspect the organic ligand is a crystal growth inhibitor.

<u>Other Corrosion Inhibitor Compounds</u>

Other suitable additional corrosion inhibitor compounds include, mercaptans and diols, especially mercaptans with 4 to 20 carbon atoms including lauryl mercaptan, thiophenol, thionapthol, thionalide and thioanthranol. Also suitable are saturated or unsaturated C_{10}-C_{20} fatty acids, or their salts, especially aluminium tristearate. The C_{12}-C_{20} hydroxy fatty acids, or their salts, are also suitable. Phosphonated octa-decane and other anti-oxidants such as betahydroxytoluene (BHT) are also suitable.

Copolymers of butadiene and maleic acid, particularly those supplied under the trade reference no. 07787 by Polysciences Inc have been found to be of particular utility as corrosion inhibitor compounds.

<u>Total Available Oxygen (AvO) Level</u>

It has been found that, for optimal anti-silver tarnishing performance, the level of available oxygen in the present compositions, measured in units of % available oxygen by weight of the composition, is preferably controlled; the level of available oxygen should hence preferably be in the range from 0.3% to 2.5%, preferably from 0.5% to 1.7%, more preferably from 0.6% to 1.5%, most preferably from 0.7% to 1.2%, measured according to the method described hereunder.

<u>Rate of Release of AvO</u>

The rate of release of available oxygen is preferably also controlled; the rate of release of available oxygen from the compositions herein preferably should be such that, when using the method described hereinafter, the available oxygen is not completely released from the composition until after 3.5 minutes, preferably the available oxygen is released in a time interval of from 3.5 minutes to 10.0 minutes, more preferably from 4.0 minutes to 9.0 minutes, most preferably from 5.0 minutes to 8.5 minutes.

Method for Measuring Level of Total Available Oxygen (AvO) and Rate of Release of AvO in a Detergent Composition

Method

1. A beaker of water (typically 2L) is placed on a stirrer Hotplate, and the stirrer speed is selected to ensure that the product is evenly dispersed through the solution.

2. The detergent composition (typically 8g of product which has been sampled down from a bulk supply using a Pascal sampler), is added and simultaneously a stop clock is started.

3. The temperature control should be adjusted so as to maintain a constant temperature of 20°C throughout the experiment.

4. Samples are taken from the detergent solution at 2 minute time intervals for 20 minutes, starting after 1 minute, and are titrated by the "titration procedure" described below to determine the level of available oxygen at each point.

Titration Procedure

1. An aliquot from the detergent solution (above) and 2ml sulphuric acid are added into a stirred beaker

2. Approximately 0.2g ammonium molybdate catalyst (tetra hydrate form) are added

3. 3mls of 10% sodium iodide solutionare added

4. Titration with sodium thiosulphate is conducted until the end point. The end point can be seen using either of two procedures. First procedure consists simply in seeing the yellow iodine colour fading to clear. The second and preferred procedure consists of adding soluble starch when the yellow colour is becoming faint, turning the solution blue. More thiosulphate is added until the end point is reached (blue starch complex is decolourised).

The level of AvO, measured in units of % available oxygen by weight, for the sample at each time interval corresponds to the amount of titre according to the following equation

$$\frac{\text{Vol } S_2O_3(\text{ml}) \times \text{Molarity } (S_2O_3) \times 8}{\text{Sample mass (g)}}$$

AvO level is plotted versus time to determine the maximum level of AvO, and the rate of release of AvO

Controlled Rate of Release - Means

A means may be provided for controlling the rate of release of oxygen bleach to the wash solution.

Means for controlling the rate of release of the bleach may provide for controlled release of peroxide species to the wash solution. Such means could, for example, include controlling the release of any inorganic perhydrate salt, acting as a hydrogen peroxide source, to the wash solution.

Suitable controlled release means can include coating any suitable component with a coating designed to provide the controlled release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to bleach of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal sulphates, silicates and carbonates, including calcium carbonate and silicas.

A preferred coating material, particularly for an inorganic perhydrate salt bleach source, comprises sodium silicate of $SiO_2 : Na_2O$ ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of SiO_2 by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating.

Any inorganic salt coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15}-C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5×10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10}-C_{20} mono- and diglycerol ethers and also the C_{10}-C_{20} fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten

coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent.

Other means of providing the required controlled release include mechanical means for altering the physical characteristics of the bleach to control its solubility and rate of release. Suitable protocols could include compression, mechanical injection, manual injection, and adjustment of the solubility of the bleach compound by selection of particle size of any particulate component.

Whilst the choice of particle size will depend both on the composition of the particulate component, and the desire to meet the desired controlled release kinetics, it is desirable that the particle size should be more than 500 micrometers, preferably having an average particle diameter of from 800 to 1200 micrometers.

Additional protocols for providing the means of controlled release include the suitable choice of any other components of the detergent composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required controlled release kinetics to be achieved.

Heavy Metal Ion Sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline

metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates. Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof.

Crystal Growth Inhibitor Component

The detergent compositions preferably contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C_1-C_4 diphosphonic acid, more preferably a C_2 diphosphonic acid, such as ethylene diphosphonic acid, or most

preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Enzyme Stabilizing System

Preferred enzyme-containing compositions herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, chlorine bleach scavengers and mixtures thereof. Such stabilizing systems can also comprise reversible enzyme inhibitors, such as reversible protease inhibitors.

Organic Polymeric Compound

Organic polymeric compounds may be added as preferred components of the compositions in accord with the invention. By organic polymeric compound it is meant essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of molecular weight 2000-10000 and their copolymers with any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof. Preferred are the copolymers of acrylic acid and maleic anhydride having a molecular weight of from 20,000 to 100,000.

Preferred commercially available acrylic acid containing polymers having a molecular weight below 15,000 include those sold under the tradename Sokalan PA30, PA20, PA15, PA10 and Sokalan CP10 by BASF GmbH, and those sold under the tradename Acusol 45N by Rohm and Haas.

Preferred acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula -[CR_2-CR_1(CO-O-R_3)]- wherein at least one of the substituents R_1, R_2 or R_3, preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen (i.e. a methacrylic acid monomer). The most preferred copolymer of this type has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methacrylic acid.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

<u>Lime Soap Dispersant Compound</u>

The compositions of the invention may contain a lime soap dispersant compound, preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. Preferred lime soap disperant compounds are disclosed in PCT Application No. WO93/08877.

<u>Polymeric Dye Transfer Inhibiting Agents</u>

The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

Other Optional Ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

pH of the Compositions

The detergent compositions used in the present invention are preferably not formulated to have an unduly high pH, in preference having a pH measured as a 1% solution in distilled water of from 8.0 to 12.5, more preferably from 9.0 to 11.8, most preferably from 9.5 to 11.5.

Machine Dishwashing Mehod

Any suitable methods for machine washing or cleaning soiled tableware, particularly soiled silverware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

Examples

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

STPP	:	Sodium tripolyphosphate
Citrate	:	Tri-sodium citrate dihydrate
Bicarbonate	:	Sodium hydrogen carbonate
Carbonate	:	Anhydrous sodium carbonate
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 1.6-3.2)
Metasilicate	:	Sodium metasilicate (SiO_2:Na_2O ratio = 1.0)
PB1	:	Anhydrous sodium perborate monohydrate
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
Percarbonate	:	Anhydrous sodium percarbonate of nominal formula $2.Na_2CO_3.3H_2O_2$
Plurafac	:	C_{13}-C_{15} mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5, sold under the tradename Plurafac by
Tergitol	:	Nonionic surfactant available under the tradename Tergitol 15S9 from Union Carbide
SLF18B	:	Epoxy-capped poly(oxyalkylated) alcohol of Example III of WO 94/22800 wherein 1,2-epoxydodecane is substituted for 1,2-epoxydecane available under the tradename Polytergent SLF18B from OLIN.
TAED	:	Tetraacetyl ethylene diamine
HEDP	:	Ethane 1-hydroxy-1,1-diphosphonic acid
DETPMP	:	Diethyltriamine penta (methylene) phosphonate, marketed by monsanto under the tradename Dequest 2060
MnTACN	:	Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.

PAAC	:	Pentaamine acetate cobalt (III) salt
BzP	:	Benzoyl Peroxide
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
Protease	:	Proteolytic enzyme
Amylase	:	Amylolytic enzyme.
BTA	:	Benzotriazole
PA30	:	Polyacrylic acid of average molecular weight approximately 4,500
MA/AA	:	Randon copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000
480N	:	Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500
Sulphate	:	Anhydrous sodium sulphate.
pH	:	Measured as a 1% solution in distilled water at 20°C

In the following examples all levels are quoted as % by weight of the composition:

Example 1

The following compact high density (0.96Kg/l) dishwashing detergent compositions A to H were prepared in accord with the invention:

	A	B	C	D	E	F	G	H
STPP	-	-	54.30	51.40	51.4	-	-	50.90
Citrate	35.0	17.05	-	-	-	46.10	40.20	-
Carbonate	-	17.50	14.0	14.0	14.0		8.0	32.10
Bicarbonate	-	-	-	-	-	25.40	-	-
Silicate	32.00	14.81	14.81	10.0	10.0	1.04	25.0	3.10
Metasilicate	-	2.50	-	4.5	4.5	-	-	-
PB1	1.95	9.74	7.79	7.79	7.79	-	-	-
PB4	8.65	-	-	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.70	11.80	4.80
Tergitol	2.0	2.0	2.0	2.0	1.5	2.0	2.0	3.0
SLF 18B	1.50	2.0	1.45	2.0	1.50	2.60	1.90	5.30
TAED	5.22	2.39	-	-	-	2.21	-	1.40
HEDP	-	1.0	-	-	-	-	-	-
DETPMP		0.65	-	-	-	-	-	-
Mn TACN	-	-	-	-	-	-	0.008	-
PAAC	-	-	0.008	0.01	0.007	-	-	-
BzP	-	-	-	-	1.40	-	-	-
Paraffin	0.50	0.55	0.47	0.50	0.50	0.60	-	-
Protease	2.20	2.20	0.90	1.62	1.40	0.80	1.80	0.30
Amylase	1.50	1.50	0.76	1.50	1.70	1.10	2.10	0.80
BTA	0.30	0.30	0.30	0.30	0.30	-	0.30	0.30
MA/AA	-	-	-	-	-	-	4.20	-
480N	3.27	6.0	-	-	-	-		0.90
Perfume	0.20	0.20	0.20	0.20	0.20	0.20	0.10	0.10
Sulphate	7.0	20.0	5.0	2.20	5.0	12.00	4.60	2.0
misc/water to balance								
pH (1% solution)	10.8	11.0	10.8	11.3	11.3	9.6	10.8	10.9

Example 2

The following granular dishwashing detergent compositions examples I to P of bulk density 1.02Kg/L were prepared in accord with the invention:

	I	J	K	L	M	N	O	P
STPP	30.00	30.00	33.0	30.5	29.62	31.10	26.6	17.60
Carbonate	30.50	30.50	31.0	30.0	23.00	39.40	4.20	45.0
Silicate	7.40	7.40	7.50	7.21	13.30	3.36	43.70	12.44
Metasilicate	-	-	4.50	5.10				
Percarbonate	-	-	-	-	-	4.0	-	
PB1	4.40	4.25	4.50	4.50	-	-	-	
NaDCC	-	-	-	-	2.00	-	1.60	1.0
Tergitol	1.0	1.5	1.5	1.0	2.0	1.0	1.0	1.0
SLF 18B	-	1.0	0.75	0.75	1.90	0.70	0.60	-
Pluràfac	1.20							0.35
TAED	1.00	-	-	-	-	0.80	-	
PAAC	-	0.004	0.004	0.004	-	-	-	
BzP	-	-	-	1.40	-	-	-	
Paraffin	0.25	0.25	0.25	0.25	-	-	-	
Protease	1.10	0.45	0.81	0.85	-	0.30	-	
Amylase	0.38	0.38	0.70	0.76	-	0.80	-	
BTA	0.15	0.15	0.15	0.15	-	-	-	
Perfume	0.20	0.20	0.20	0.20	0.10	0.20	0.20	
Sulphate	22.0	22.0	16.0	18.50	30.08	19.34	23.1	23.6
Misc/water to balance								
pH (1% solution)	10.80	10.80	11.3	11.3	10.70	11.5	12.7	10.9

Example 3

The following tablet detergent composition examples Q to V in accord with the present invention were prepared by compression of a granular dishwashing detergent composition at a pressure of $13KN/cm^2$ using a standard 12 head rotary press:

	Q	R	S	T	U	V
STPP	-	48.80	49.20	30.0	-	46.80
Citrate	26.40	-	-	-	31.10	-
Carbonate	-	5.0	14.0	15.40	14.40	23.0
Silicate	26.40	14.80	15.0	12.60	17.70	2.40
Protease	1.76	2.20	1.26	1.0	1.60	0.40
Amylase	1.20	1.50	1.50	0.85	2.0	0.30
PB1	1.56	7.69	12.20	10.60	15.70	-
PB4	6.92	-	-	-	-	14.40
Tergitol	2.0	2,0	2.0	2.0	2.0	2.0
SLF 18B	2.0	2.0	2.0	2.0	1.0	6.30
PAAC	-	-	0.016	0.009	-	-
MnTACN	-	-	-	-	0.007	-
TAED	4.33	2.50	-	-	1.30	1.84
HEDP	0.67	-	-	0.7	-	0.40
DETPMP	0.65	-	-	-	-	-
Paraffin	0.42	0.50	0.5	0.55	-	-
BTA	0.24	0.30	0.3	0.33	-	-
PA30	3.2	-	-	-	-	-
MA/AA	-	-	-	-	4.51	0.55
Perfume	-	-	0.05	0.05	0.20	0.2
Sulphate	24.05	13.0	8.0	18.7	10.68	10.0
Misc/water to balance						
weight of tablet	25g	25g	20g	30g	18g	20g
pH (1% solution)	10.60	10.60	10.7	10.7	10.9	11.2

WHAT IS CLAIMED IS:

1. An automatic dishwashing detergent composition comprising
   a) one or more high cloud point nonionic surfactants having a cloud point of greater than 40°C;
   b) an amount of water-soluble salt to provide conductivity in deionised water measured at 25°C of greater than 3 milli Siemens/cm.

2. An automatic dishwashing detergent composition according to claim 1 wherein the nonionic surfactant comprises greater than 8 carbon atoms.

3. An automatic dishwashing detergent composition according to either of claims 1 or 2 wherein the nonionic surfactant is an alkoxylated surfactant comprising alkoxylated groups selected from ethyleneoxy, propyleneoxy and butyleneoxy groups.

4. An automatic dishwashing detergent composition according to any of claims 1 to 3 wherein the nonionic surfactant on average comprises greater than 6 moles of ethyleneoxide.

5. An automatic dishwashing detergent composition according to any of claims 1 to 5 wherein the nonionic surfactant has a cloud point of greater than 50°C.

6. An automatic dishwashing detergent composition according to any of claims 1 to 5 wherein the nonionic surfactant is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol comprising from 8 to 20 carbon atoms and on average from 6 to 15 moles of ethyleneoxide per mole of alcohol or alkyl phenol.

7. An automatic dishwashing detergent composition according to any of claims 1 to 6 wherein the water-soluble salt is a water-soluble sulphate, silicate, carbonate or bicarbonate salt.

8. An automatic dishwashing detergent composition according to any of claims 1 to 7 additionally comprising a suds suppresser.

9. An automatic dishwashing detergent composition according to claim 8 wherein the suds suppresser is a low cloud point nonionic surfactant.

10. An automatic dishwashing detergent composition according to claim 9 wherein the low cloud point nonionic surfactant has the general formula:

$$R_1O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_y[CH_2CH(OH)R_2] \quad (I)$$

wherein R_1 is a linear or branched, aliphatic hydrocarbon radical having from 4 to 12 carbon atoms including mixtures thereof; R_2 is a linear or branched aliphatic hydrocarbon radical having from 2 to 10 carbon atoms including mixtures thereof; x is an integer having an average value of from 0.5 to 1.5; and y is an integer having a value of least 20.

11. An automatic dishwashing detergent composition according to any of claims 1 to 10 wherein the conductivity in deionised water measured at 25°C is greater than 4 milli Siemens/cm.

12. A method of washing dishware in an automatic dishwasher by contacting the dishware with a solution comprising a high cloud point nonionic surfactant having a cloud point of greater than 40°C and an amount of water-soluble salt which provides conductivity of greater than 3 milli Siemens/cm at temperatures less than 40°C.

13. Use of an automatic dishwashing detergent composition according to any of claims 1 to 11 for cleaning greasy soils from dishware.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/15977

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 1/70, 1/72, 1/722, 3/04, 3/08
US CL :510/221, 224, 228, 421
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/221, 224, 228, 421

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS
search terms: tergitol 15s9, rhodasurf tmd 8.5, neodol 91-8, automatic dishwasher, silicate, sulphate, perborate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,162,987 A (MAGUIRE, JR. ET AL) 31 July 1979, See Abstract; column 5, line 30 to column 8, line 60; column 12, lines 43-69, column 15, line 50 to column 17, line 10.	1-3
X	US 5,362,413 A (KAUFMANN ET AL)08 November 1994, See Abstract; column 3, lines 25-40; column 7, lines 20-69; column 9, lines 1-25; column 13, line 15 to column 15, line 50.	1-3
X	US 5,540,866 A (ASZMAN ET AL) 30 July 1996, See Abstract; column 2, lines 40-69; column 4, line 50 to column 5, line 63.	1-3
X	US 5,458,802 A (SANDERSON ET AL) 17 October 1995, See Abstract; column 3, line 65 to column 4, line 15; column 6, lines 20-35; column 9, line 60 to column 10, line 10.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

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22 OCTOBER 1997

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INTERNATIONAL SEARCH REPORT

International application No. PCT/US97/15977

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-13
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.